

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representation of
The original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

THIS PAGE BLANK (USPTO)

(19)



Eur päisches Patentamt
Europ an Patent Office
Office européen des br vets



(11) Publication number : **0 628 593 A1**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number : **94303652.5**

(51) Int. Cl.⁵ : **C08J 5/18, B29C 55/00,
B32B 27/08, B65D 65/40,
C08L 29/04, C08L 23/08**

(22) Date of filing : **20.05.94**

(30) Priority : **20.05.93 US 65316**

(43) Date of publication of application :
14.12.94 Bulletin 94/50

(84) Designated Contracting States :
**AT BE CH DE DK ES FR GB GR IE IT LJ LU NL
PT SE**

(71) Applicant : **W.R. GRACE & CO.-CONN.**
1114 Avenue of the Americas
New York New York 10036 (US)

(72) Inventor : **Bekele, Solomon**
4 Walden Way
Taylors, SC 29687 (US)

(74) Representative : **Bentham, Stephen**
J.A. KEMP & CO.
14 South Square
Gray's Inn
London WC1R 5LX (GB)

(54) **Blends of EVOH and terpolymers of ethylene, acrylic ester and maleic anhydride or glycidyl methacrylate and products thereof.**

(57) **A highly orientable heat-shrinkable film with low oxygen permeability comprises at least one oxygen barrier layer formed of a blended resin of ethylene vinyl alcohol and a terpolymer of ethylene, an acrylic ester, and a third compound selected from the group consisting of maleic anhydride and glycidyl methacrylate.**

EP 0 628 593 A1

Field of the Invention

The present invention relates to the plasticization of ethylene vinyl alcohol, and in particular relates to a chlorine free heat shrinkable plastic film for which the predominant oxygen barrier layer is formed of ethylene vinyl alcohol and a plasticizing terpolymer.

Background of the Invention

In the packaging and delivery of certain food products, such as cheese, pork, smoked and processed meats, and particularly fresh red meat, there exists the need to protect the meat for the period of time from when it is first butchered until it is used by the end consumer. In particular, because oxygen promotes microbial degradation in such meats, the most pertinent requirement for protecting fresh red meat is long term protection against oxygen.

One excellent material for preventing the passage of oxygen is thin, but multilayer sheet wrapping material or film in which the oxygen barrier is formed of one or more layers of polyvinylidene chloride, which is also referred to as "PVDC" or "saran". As its name implies, however, one of the key ingredients of PVDC is chlorine. There presently exist a number of reasons, including environmental considerations, that make the elimination of chlorine desirable in such sheet wrap materials.

Accordingly, other materials have been included in sheet wrap materials to provide the oxygen barrier. One material which has good oxygen barrier characteristics under certain conditions is ethylene vinyl alcohol, often abbreviated as "EVOH". EVOH, however, tends to lose its oxygen barrier properties when subjected to moisture. As would be expected, fresh red meats and similar food products contain high amounts of moisture which in turn tend to degrade the otherwise useful oxygen barrier properties of EVOH.

Another requirement of such a film is that it be physically strong. In this regard, certain olefin products such as polypropylene and polyethylene form sheet materials with excellent strength characteristics, but which tend to have relatively high oxygen transmission rates. Accordingly, multilayer plastic films often include polyolefin layers for strength in combination with layers of other materials that have better barrier characteristics.

As implied by the designation "heat shrinkable", another desirable property of the film is that it be compatible with heat shrinking processes that are often used in conjunction with such films. As is known to those familiar with heat shrinkable products and processes, the term "orientation" is used to refer to various deformation processes carried out on plastic film materials during their manufacture. The viscous and elastic properties of most thermoplastic polymers enable those polymers to recover from deformation or to otherwise "remember" both the nature of the orientation and the temperature at which the original orientation takes place. As a result, a plastic material that is oriented at a certain temperature (e.g. 200°F), and then cooled to ambient or working temperatures will, if later reheated to temperatures approaching the deformation temperature (again 200°F), similarly have a tendency to return to its pre-oriented state at that temperature. If the orientation is an expansion process, then the recovery will be a shrinking process. Thus, a further desirable property of an oxygen barrier packaging film is that it can be oriented at relatively moderate temperatures, and then subsequently shrunk at those moderate temperatures.

Stated differently, packagers prefer to carry out the heat shrink process at temperatures well below those at which red meat would start to cook. Thus, the lower the temperature at which a plastic can be oriented, the correspondingly lower temperature at which it can be heat shrunk. Additionally, the greater the degree to which a plastic film can be oriented, the greater--and usually more useful--the degree to which it will shrink. Therefore, the greater the ratio at which a particular film can be oriented, the better its heat shrink properties at all temperatures, and particularly at lower ones.

As further stated above, as a replacement for chlorinated materials such as PVDC, EVOH is another excellent oxygen barrier material at low relative humidities or other measures of moisture content. Similarly, it eliminates the use of chlorine. At higher moisture contents, however, the oxygen barrier properties of EVOH rapidly decrease. As a result, when EVOH is used as an oxygen barrier, it must be part of a composite structure that otherwise prevents moisture from interfering with the oxygen barrier properties of the EVOH.

Furthermore, as previously noted, heat shrinkable properties are desirable in plastic film of this type, and the degree to which a film can be heat shrunk is a function of the extent to which it can be originally deformed (at a given temperature) while maintaining its integrity.

In my co-pending application, Serial No. 970,896, filed November 3, 1992, I describe improved multilayer films using EVOH as a barrier layer. The contents of Serial No. 970,896 are incorporated entirely herein by reference. Prior to my co-pending application, the orientability of EVOH composite films never exceeded a factor of about 8 to 1, usually expressed as 8 x 1, when oriented at or below 212°F. As known to those familiar with the manufacture of such films, the orientation ratio is the multiplication product of the extent to which the

plastic film material is expanded in several directions, usually two directions perpendicular to one another. These directions are frequently referred to as the machine direction ("MD") which is the direction in which the extruded material is formed, and the transverse direction ("TD") which is the direction transverse or perpendicular to the machine direction. The degree of orientation is also referred to as the orientation ratio, or sometimes as the "racking ratio".

Additionally, in comparison to the usual structural components of a multilayer film, EVOH often has the highest glass transition temperature (T_g). As is known to those familiar with polymer materials, a higher T_g makes a polymer less subject to orientation. As a result, when EVOH is included in a multilayer film, it is often the least plastic, least orientable of the components and thus the limiting factor in the amount to which the overall film can be oriented.

Object and Summary of the Invention

Therefore, it is an object of the present invention to increase the plasticity of EVOH and to correspondingly provide a highly orientable heat-shrinkable film with low oxygen permeability, even at higher relative humidities.

The invention meets this object with a multilayer film that comprises at least one oxygen barrier layer formed of a blended resin of a barrier polymer such as ethylene vinyl alcohol and a terpolymer of ethylene, acrylic ester, and either maleic anhydride or glycidyl methacrylate.

In another aspect, the invention comprises a method of producing a highly orientable, heat-shrinkable, multi-layer film with low oxygen permeability.

In yet another aspect, the invention comprises a method of packaging food products that are sensitive to exposure to oxygen in a manner that will protect those food products against oxygen for satisfactory time periods.

In yet another aspect, the invention is a method of increasing the plasticity of ethylene vinyl alcohol, or other oxygen-barrier polymers that have higher glass transition temperatures.

The foregoing and other advantages of the invention will be more clearly illustrated when taken in conjunction with the detailed description and the accompanying drawings in which:

Description of the Drawings

Figure 1 is a cross-sectional view of a multi-layer film according to the present invention.

Detailed Description

The invention is a highly orientable heat-shrinkable film with low oxygen permeability. The film comprises at least one barrier layer formed of a blended resin of ethylene vinyl alcohol and a terpolymer of ethylene, an acrylic ester, and a third compound selected from the group consisting of maleic anhydride (MAH) and glycidyl methacrylate (GMA).

Ethylene vinyl alcohol (EVOH) is used herein to describe a polymer formed of ethylene and hydroxyl (OH) functional groups. EVOH materials are often characterized by their percentage content of ethylene molecules, also referred to as the ethylene mole fraction. EVOH is commercially available with ethylene mole fractions of about 27% to about 48%. In the preferred embodiment of the invention, the ethylene mole fraction of the EVOH layer is between about 30% and 50% of the EVOH polymer, and in the most preferred embodiments, the ethylene fraction is about 44%. Generally speaking, a higher ethylene mole fraction gives better orientation, while a lower ethylene mole fraction offers better oxygen barrier characteristics. Thus, the selection is often made for the particular combination of properties desired in a manner well understood by those familiar with these materials and of skill in this art.

Suitable EVOH resins are available from Evalca, 1001 Warrensville Road, Suite 201, Lisle, Illinois, 60632; and from Morton International, 1275 Lake Avenue, Woodstock, Illinois, 60098.

As used herein, the terpolymers have the structures illustrated below:



30

35

40

45

50

55

The skin layer 17 can be selected from the group consisting of blends of ethylene vinyl acetate and high density polyethylene (HDPE), polypropylene homopolymers, copolymers or terpolymers, and blends of linear low density polyethylene and preferably metallocene polyolefins.

As used herein, the designation metallocene polyolefins refers to a group of olefin polymers that are produced using metallocene catalysts. Metallocene olefin polymers are characterized by narrower or more homogeneous compositional properties such as molecular weight distribution than are polymer resins produced by more conventional Ziegler-Natta catalyst systems. Conventional Ziegler-Natta catalyst polymerization systems have discrete composition differences which are manifested as different catalyst reaction sites. Each such site has a different reaction rate and selectivity. In contrast, metallocene catalyst systems are characterized by a single identifiable chemical type which has a singular rate and selectivity. Thus, conventional Ziegler-Natta catalyst systems produce resins that reflect the differential character of the different catalyst sites. Alternatively and advantageously, metallocene catalyst systems produce polymer resins that reflect a single type of catalytic site. It will be noted by those familiar with polymer resins, however, that at least some previously available ethylene-based linear polymers approximated the physical and compositional properties achieved by the metallocene catalyst polyolefins. Stated differently, traditional Ziegler-Natta catalyzed polymerization processes operating at low reaction rates can produce relatively homogeneous resins that compare favorably with the homogeneity of metallocene catalyzed resins. Exemplary Ziegler-Natta catalyzed polyolefin resins are sold under the trade name Tafmer® by Mitsui Petrochemicals Americas, Ltd., 250 Park Avenue, Suite 950, New York, N.Y., 10177. Exemplary metallocene-catalyzed polyolefin resins are sold under the trade name Ex-act® by Exxon Chemicals Company, P.O. Box 3272, Houston, Texas 77253.

Accordingly, although illustrated as a complete structure, Figure 1 can also illustrate a substrate and a coating on the substrate. The substrate comprises the sealant layer 11, the core layer 12, and the first tie layer 13. The coating comprises of another tie layer 14, and oxygen barrier layer 15, another tie layer 16, and the skin layer 17.

In preferred embodiments, the barrier layer 15 is formed of a blended resin in which the ethylene vinyl alcohol--preferably 44% mole fraction ethylene--makes up between about 85% and 90% by weight and the ethylene, acrylic ester, and maleic anhydride terpolymer makes up between about 10% and 15% by weight.

In a presently preferred embodiment that is exemplary of commercial food wraps, the invention is incorporated in a film of 24 mils thickness. In this structure, the sealant layer (11) is 3.0 mils thick, the core is 9.0 mils, each tie layer is 1.2 mils, the blend is 2.4 mils, and the skin layer is 6.0 mils thick.

One of the advantages of the barrier layer of the present invention is its ability to be bi-axially oriented at relatively high ratios. As noted above, films according to the present invention have a typical commercial thickness of about 24 mils (1 mil equals 0.001 inch). Using the present invention, such films can have bi-axial orientation ratios of at least 10 to 1 and to date have been oriented at ratios of as high as almost 15 to 1. In turn, such films have been demonstrated to have normalized oxygen transmission rates (OTR's) at 0% relative humidity (RH) of between about 2 and 12 cm³-mil/day/m²-atm at room temperature, and an OTR at 100% RH of between about 19 and 42 cm³-mil/day/m²-atm at room temperature.

A summary of some of these various properties are included in the two following tables. Table 1 shows the orientation properties and Table 2 illustrates the barrier properties of various samples of the present invention.

TABLE 1: ORIENTATION PROPERTIES

Sample	Variable ¹	Orientation MD x TD	Orientation Total
Control	100/0	Less than 3.0 x 2.5	Less Than 7.5
3525	85/15 3200	3.3 x 3.2	10.6
3697 (#12)	80/20 3200	3.2 x 3.72	11.9
3698 (#13)	85/15 3700	2.78 x 3.72	10.3
3699 (#14)	85/15 3410	3.2 x 3.72	11.9
3700 (#15)	85/15 3200	3.20 x 3.72	11.9
3701 (#16)	90/10 3200	2.76 x 3.72	10.3
3702 (#17)	90/10 3200	N/A	N/A
3703 (#21)	85/15 3410	3.20 x 3.72	11.9
3748 (A-2)	85/15 3410	3.20 x 3.72	11.9
3760 (#9)	85/15 3410	3.20 x 3.72	11.9
3761 (#10)	85/15 3410	3.20 x 3.72	11.9

¹Weight Percent of EVOH/Terpolymer; Elf Atochem Product No.

In all cases EVOH is Eval E105 and Terpolymer is a Lotader product having the number indicated; the terpolymers are all maleic anhydride terpolymers.

TABLE 2: BARRIER PROPERTIES

Sample	Blend % EVOH/ Terpolymer	Tensile ¹	Elong.	Modulus	MVTR ²	Normalized RT OTR ³	
						0% RH	100% RH
4634	100/0	11,017	171	41472	1.32	2.2	27.8
4635 ⁴	90/10	11847	189	32399	1.34	3.6	35.4
4636	85/15	11704	200	27387	1.34	8.2	19.0
4637	80/20	11640	196	27364	1.38	12.0	41.7
4638 ⁵	90/10	10894	186	30768	1.37	7.30	35.0
4639	85/15	11098	186	25277	1.45	30.8	65.0
4640	80/20	11364	185	25530	1.45	87.9	96.4
4641	75/15	10876	176	13799	1.42	27.4	61.2

¹. Tensile, Elongation, and Modulus are computed as the average of lengthwise and transverse values for each

². Moisture Vapor Transmission Rate (g/24 hours-100in² at 100°F and 100% relative humidity)

³. Oxygen Transmission Rate (cm³-mil/day/m²-atm at room temperature)

⁴. Nos. 4635-4637 used maleic anhydride terpolymer

⁵. Nos. 4638-4641 used glycidyl methacrylate terpolymer

The invention further comprises the method of producing a highly orientable heat-shrinkable multi-layer film with low oxygen permeability. The method comprises blending an ethylene vinyl alcohol resin with a terpolymer of ethylene, and acrylic ester, and a third compound selected from the group consisting of maleic anhydride and glycidyl methacrylate. Thereafter, the resulting blended resin is incorporated as a layer in a multi-layer plastic film.

As mentioned earlier, and in accordance with conventional techniques, the step of incorporating the blended resin can comprise applying the blended resin as a coating onto the tie layer of a substrate formed of a sealant layer, a core layer on the sealant layer, and the tie layer on the core layer. Typically, the substrate is coextruded as the sealant, core and tie layers prior to the step of applying the blended resin to the substrate. As illustrated in Figure 1, the method can further comprise the step of applying the second tie layer 14 to the substrate tie layer 13 prior to the step of applying the blended resin.

The method can then further comprise the steps of applying the third tie layer 16 to the blended resin layer 15 after the blended resin layer 15 has been applied to the substrate and thereafter coating the third tie layer 16 with the skin layer 17.

As is known to those familiar with the manufacture of such films, the substrate can be beneficially irradiated to enhance its properties, typically crosslinking, prior to the step of applying the coating layers to it.

Alternatively, the entire multi-layer film such as illustrated in Figure 1 can be coextruded to form the entire structure in one step and then irradiated.

The method of forming the film can then further comprise the step of bi-axially orienting the multi-layer plastic film. As known to those familiar with such techniques, a typical orientation would include maintaining the film at a temperature of between about 160 and 210 F, preferably 165 and 210 F, while expanding the film in both the machine and transverse directions, and thereafter cooling the film to about 45°F while maintaining the film in the expanded condition to maintain its orientation.

Other than the composition of the film, the extrusion, irradiation and coating steps (or the coextrusion steps) are conventional to those of ordinary skill in this art, as is the equipment used, and will not otherwise be described in detail herein. As a brief summary, however, the core and sealant layers that form the substrate are extruded at appropriate temperatures; e.g. approximately 350-400°F for the composite films of the present invention. The substrate is quenched at about 50°F and then irradiated. The coating layers are then applied by extrusion, at temperatures of about 330-430°F, and again quenched to about 50°F. The product is a flattened tube of composite film that is referred to as the tape. The tape is then heated in a water bath to a temperature of between about 165° and 210°F, nipped (on rolls), and directed through an air ring. The air ring inflates the tape, while a terminal set of nip rolls draw it at a higher rate than it is initially fed. As a result, the air ring helps expand the tape in the transverse direction into a tube while the terminal nip rolls expand it in the machine direction. The terminal nip rolls also re-flatten the tubing, after which it is wound for use or other processing.

The film of the invention can then be used in an appropriate method of wrapping a food product in the highly oriented heat-shrinkable multi-layer film, and then heat-shrinking the multi-layer film around the food product to complete the package.

As is further known to those familiar with this type of packaging, the heat-shrinking step typically comprises immersing the wrapped food product in a shrink tunnel having a temperature of between 160° and 210°F--i.e., corresponding to the orientation temperature--for a time period sufficient for the oriented film to shrink to a substantially unoriented condition, while brief enough to prevent the shrink tunnel from affecting the properties of the food product.

In another aspect, the invention comprises a method of increasing the plasticity of ethylene vinyl alcohol, for a variety of purposes, in which the method comprises blending the ethylene vinyl alcohol with a functionally effective amount of a terpolymer of ethylene, an acrylic ester, and a third compound selected from the group consisting of maleic anhydride and glycidyl methacrylate. In the preferred embodiment, the terpolymer includes maleic anhydride, and is blended in an amount of between 10% and 25% with the ethylene vinyl alcohol.

Although 44% EVOH has been used in the preferred embodiments herein, the invention should also help improve the orientability of the lower ethylene mole fraction grades of EVOH (i.e., those grades that are less plastic, but better O₂ barriers) in any areas where plastization is required, including injection molding, thermoforming, or other finishing processes. Similarly, the invention should offer increased plasticity and related advantages in any process where glass transition temperature is a limiting factor.

In the drawings and specification, there have been disclosed typical preferred embodiments of the invention and, although specific terms have been employed, they have been used in a generic and descriptive sense only, and not for purposes of limitation, the scope of the invention being set forth in the following claims.

Claims

1. A plastic film with low oxygen permeability, said film comprising:
 at least one oxygen barrier layer formed of a blended resin of
 a terpolymer of ethylene, an acrylic ester, and a third compound selected from the group consisting
 of maleic anhydride and glycidyl methacrylate; and
 an oxygen-barrier polymer that has a glass transition temperature greater than the glass transition
 temperature of the terpolymer.
2. A film according to claim 1 wherein the weight percentage of said oxygen-barrier polymer in said blended
 resin is from 85 to 90 percent.
3. A highly orientable heat-shrinkable film with low oxygen permeability, said film comprising at least one
 oxygen barrier layer formed of a blended resin of ethylene vinyl alcohol and a terpolymer of ethylene, an
 acrylic ester, and a third compound selected from the group consisting of maleic anhydride and glycidyl
 methacrylate.
4. A film according to claim 3 wherein the weight percentage of ethylene vinyl alcohol in said blended resin
 is greater than 50 percent.
5. A film according to claim 4 wherein the weight percentage of ethylene vinyl alcohol in said blended resin
 is from 85 to 90 percent.
6. A film according to claim 3, 4 or 5 wherein the ethylene content of said ethylene vinyl alcohol is about 44
 mole percent.
7. A film according to any one of the preceding claims which is a multilayer film.
8. A film according to claim 7 wherein said multilayer film comprises a substrate portion and a coating por-
 tion.
9. A film according to claim 8 wherein said substrate portion comprises a plurality of individual layers and
 said coating portion comprises a plurality of individual layers.
10. A film according to claim 9 wherein said substrate comprises a sealant layer, a core layer and a substrate
 tie layer; and
 said coating comprises a second tie layer, an oxygen barrier layer, a third tie layer, and a skin layer.
11. A multilayer film according to claim 10 wherein said sealant layer is selected from the group consisting
 of: very low density polyethylene, linear low density polyethylene, ethylene vinyl acetate, and combina-
 tions thereof.
12. A multilayer film according to claim 10 or 11 wherein said core layer is selected from the group consisting
 of: ethylene vinyl acetate, linear low density polyethylene, and combinations thereof.
13. A multilayer film according to claim 10, 11 or 12 wherein said tie layers are selected from the group con-
 sisting of: ethylene vinyl acetate, blends of linear low density polyethylene and maleic anhydride, and
 blends of acrylic esters and maleic anhydride.
14. A multilayer film according to any one of claims 10 to 13 wherein said skin layer is selected from the group
 consisting of: blends of ethylene vinyl acetate and high density polyethylene, polypropylene monopoly-
 mers, copolymers, or terpolymers; and blends of linear low density polyethylene and metallocene polyo-
 lefins.
15. A film according to any one of the preceding claims having a biaxial orientation ratio of at least 10:1 when
 0.61 mm (24 mil) thick.
16. A film according to claim 15 that has been biaxially oriented at a ratio of from 10:1 to 15:1.
17. A film according to any one of the preceding claims wherein said third compound comprises glycidyl me-

- 50
- 55

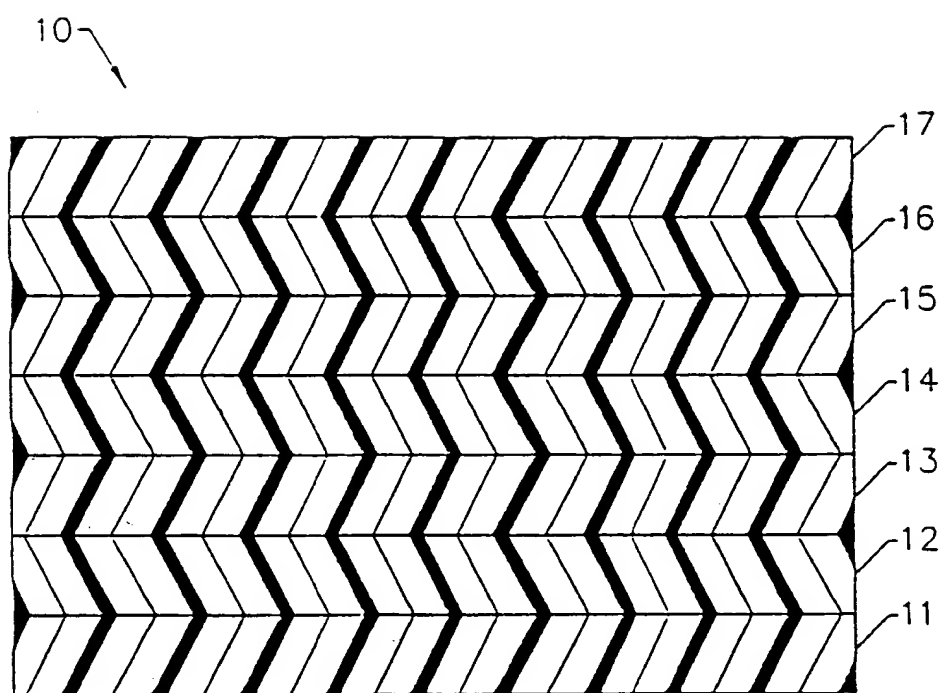


FIG. 1.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 30 3652

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	EP-A-0 177 762 (KURARAY CO., LTD.) * page 6, paragraph 2 - page 7, paragraph 2 * * page 8, last paragraph - page 9, paragraph 2 *	1-9, 19, 20	C08J5/18 B29C55/00 B32B27/08 B65D65/40 C08L29/04 C08L23/08
Y	* page 9, last paragraph - page 10, line 22; claims 1,4-6; example 3 *	10-16, 21,23-25	
Y	EP-A-0 322 199 (W.R. GRACE & CO.-CONN.) * page 6, line 1 - line 20; figure 4 *	10-14	
Y	EP-A-0 251 770 (W.R. GRACE & CO.) * column 7, line 11 - line 15; claims 1,11,14 *	15,16, 21,23-25	
Y	DE-A-32 33 693 (AMERICAN CAN CO.) * page 16, paragraph 1 * * page 21, line 29 - page 29, line 32; claims 18-38,55 *	21,23-25	
A	EP-A-0 238 870 (KURARAY CO. LTD., NIPPON PETROCHEMICALS CO.,LTD.) * claim 13 *	1	C08J C08L B65D B32B
A	EP-A-0 470 486 (E.I. DU PONT DE NEMOURS AND COMPANY) * page 2, line 36 - page 3, line 29; claim 1 *	1	
A	WO-A-93 02139 (E.I. DU PONT DE NEMOURS AND COMPANY) * claims 1,28-32 *	1	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 25 August 1994	Examiner Van Nieuwenhuize, O
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons @ : member of the same patent family, corresponding document</p>			

EPO FORM 1503 (01.92) (P01031)